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(54) MANUFACTURE OF GLASS COATED WITH MULTIFUNCTIONAL PHOTOCATALYTIC MEMBRANE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a coating onto the glass substrate which expresses phtocatalytic activity and affords hydrophilicity and stainproof property effectively decomposing contaminated organic materials adhering to the surface of the glass substrate without affecting proprietary functions of reflecting heat wave and durability.
SOLUTION: This method comprises the following steps of spraying a solution comprising a titanium compound onto the surface of a glass substrate heated at the temperature of 500° C or higher, forming a primary coating comprising titanium oxide of 40 to 100 nm thickness through thermal decomposition followed by reheating at the temperature of 550 to 650° C to form a secondary coating comprising titanium oxide.

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CLAIMS

[Claim(s)]
[Claim 1]A manufacturing method of multifunctional photocatalyst membrane covering glass reheating the first titanium oxide film that has 40-100 nm of thickness covered on a glass substrate in temperature of 550-650 **, and forming the second titanium oxide film.
[Claim 2]A manufacturing method of the multifunctional photocatalyst membrane covering glass according to claim 1 which the first titanium oxide film carries out spray spraying of the solution which becomes the glass substrate surface heated at not less than 500 ** from a titanium compound, and is characterized by a pyrolysis and making it come to form membranes.
[Claim 3]A manufacturing method of the multifunctional photocatalyst membrane covering glass according to claim 1 or 2 with which light reflectance (the film surface side) is characterized by 25 to 35% and solar reflectance (the film surface side) having the heat ray reflection performance which is 20 to 30%.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the manufacturing method of the high durability multifunctional photocatalyst membrane covering glass which has a suitable heat ray reflex function for a structural windowpane, the windowpane for vehicles, etc., an antifouling function, and a visibility improvement function by hydrophilic nature.
[0002]
[Description of the Prior Art]By high reflexivity [in / in that the heat reflective glass by a titanium oxide film covers the heat ray in the sunrays which enter from the window of a building or a vehicle, and is used for mitigation of cooling load **** / a visible range]. It is effective in making it hard to be visible in the interior of a room, and protecting privacy, many things are developed until now, and it applies also for many patents. . For example, in JP,54-122321,A, have one octylene glycol and acetylacetone as chelate ligand. Or the pyrolysis of the titanium compound which has at least one isopropoxy group or a butoxy group is carried out in a glass surface, and the method of forming a tunic is indicated in titanium oxide.
[0003]
[Problem(s) to be Solved by the Invention]However, the sheet glass with which the titanium oxide film indicated to said JP,54-122321,A was covered is used for the windowpane of a building, etc., When it constructs so that a tunic side may be exposed to the outdoors side, since a tunic side is irregular compared with the usual glass surface, it can be [that the pollutant in the atmosphere adheres easily] hard to take again. Not only with the glass with which the titanium oxide film was covered but with usual glass, sealing agents, such as silicon sealant used when sheet glass is fixed to a window frame, may carry out degradation with the passage of time, the organic matter contained in a sealing agent may flow and fall with storm sewage, and the appearance of glass may be spoiled remarkably.
[0004]
[Means for Solving the Problem]By making this invention in view of a technical problem mentioned above, reheating the first titanium oxide film that has 40-100 nm of thickness covered on a glass substrate in temperature of 550-650 **, and making the second titanium oxide film form, Multifunctional photocatalyst membrane covering glass which combined antifouling property into which a contamination organic substance which makes a photocatalyst activity function reveal and adheres to the glass substrate surface is made to disassemble effectively, and hydrophilic nature is provided without spoiling a heat ray reflex function and endurance which are equipped conventionally.

[0005]That is, a manufacturing method of multifunctional photocatalyst membrane covering glass of this invention reheats the first titanium oxide film that has 40-100 nm of thickness covered on a glass substrate in temperature of 550-650 **, and forms the second titanium oxide film.
[0006]The first titanium oxide film carries out spray spraying of the solution which becomes the glass substrate surface heated at not less than 500 ** from a titanium compound, and a manufacturing method of multifunctional photocatalyst membrane covering glass of this invention is characterized by a pyrolysis and making it come to form membranes.
[0007]As for a manufacturing method of multifunctional photocatalyst membrane covering glass of this invention, 25 to 35% and solar reflectance (film surface side) have the heat ray reflection performance which is 20 to 30%, as for light reflectance (film surface side).

[0008]
[Embodiment of the Invention]The manufacturing method of the multifunctional photocatalyst membrane covering glass of this invention can be manufactured, for example by the following processes.
(1) Spray spraying of the solution which becomes the glass substrate surface heated at 500 or more ** from a titanium compound is carried out, a pyrolysis - membrane formation — carrying out — making — thickness — 40 - 100 — nm — having — primary — a titanium oxide film — covering — a process — (— two —) — primary — a titanium oxide film — 550 - 650 — ** — temperature — reheating — things — secondary — a titanium oxide film — forming — a process .
[0009]As a titanium compound which can be used for this invention, As an inorganic titanium compound, as titanium tetrachloride and an organic titanium compound, titanium propoxyoctylene glycolate, There are dipropoxybis acetylacetonato titanium, titanium stearate, titanium isopropoxy octylene GURIKOKISHI diacetyl acetonate, etc. By carrying out spray spraying on the glass substrate surface heated by not less than 500 ** mentioned later, the pyrolysis of the solution which consists of these compounds can be carried out, and it can form a titanium oxide film. As the aforementioned diluent solvent, for example Hydrocarbon and halogenated hydrocarbon, That the glass substrate temperature at the time of what does not contain moisture, such as alcohols, ether, ketone, ester species, and fatty acid, forming said first desirable titanium oxide film shall be not less than 500 **, If it is below 500 ** in substrate temperature, while the pyrolysis of an organic titanium compound will not happen efficiently, but becoming a tunic containing undecomposed residue and reducing bond strength and appearance remarkably, it is for a photocatalyst activity function and a heat ray reflex function also falling. The range of 530-630 ** is more preferred, and when it is not less than 630 **, modification of a glass substrate may take place, and substrate temperature may spoil appearance remarkably in image distortion etc., and is not preferred.
[0010]Next, the glass substrate with which the first titanium oxide membrane was covered is reheated in temperature of 550-650 **, and the second high crystalline titanium oxide film is made to form more. Photocatalyst activity function sufficient since the crystallinity of the titanium oxide film formed as it is below 550 ** in temperature does not become high does not take place, It is because the fall of the crystallinity of the titanium oxide film by elution of the alkali component contained in a glass substrate or transition to the rutile form crystal of the anatase form crystal of titanium oxide takes place in the case of the temperature over 650 ** and sufficient photocatalyst activity function stops being revealed. Although it does not limit especially as retention time of reheating, for 5 to 15 minutes is more preferably good for more than 5 minutes. Even if it exceeds for 15 minutes in case of less than for 5 minutes, or crystallinity does not increase, and crystallinity does not increase any more, productivity worsens.
[0011]The thickness of the titanium oxide film obtained by this invention, Even if it reheats at the aforementioned temperature of 550-650 ** with it being required to be 40-100 nm, and it being the thickness below 40 nm, the crystallinity of titanium oxide does not increase, if a heat ray reflex function also falls and 100-nm thickness is exceeded while sufficient photocatalyst activity function is not revealed, a photocatalyst activity function will increase, but the excitation purity of a reflected color becomes high and the interference color of a chromatic color appears — an exterior — it is not desirable. Visible light solar radiation reflection performance falls.
[0012]The second high crystalline titanium oxide film obtained by the above reheating methods, Even when hydrophilic nature will be maintained by the surface of this tunic and dirt, such as exhaust gas and dust, adheres temporarily, a part for organicity is decomposed by a photocatalyst effect, and. Since this tunic surface is hydrophilic nature, by rain or pouring water artificially, water pours in between the tunic surface and dirt, and dirt floats, and flows and comes off.
[0013]The photocatalyst coating covering glass obtained by the method of this invention, The outstanding hydrophilic nature in which the angle of contact seven days after setting to the evaluation of hydrophilic maintenance nature mentioned later maintained not less than 30 degrees, In photocatalyst activity evaluation, the variation of peak intensity has ten or more outstanding antifouling property and the high durability which maintained the balance which solar radiation ******** (film surface side) combines further.
[0014]The photocatalyst coating covering glass which has the second high crystalline titanium oxide film obtained by this invention, When the ultraviolet rays included in sunlight, a fluorescent lamp, etc.

are irradiated, while the operation (called an oxidative degradation type reaction) which disassembles the organic matter which adhered to this tunic surface according to the photocatalyst effect, and keeps the surface of a tunic pure is shown, Hydrophilization (called a super-hydrophilic nature type reaction) also of the surface of the titanium oxide crystal itself is carried out, and the variation of peak intensity has ten or more outstanding antifouling property in the outstanding hydrophilic nature in which the angle of contact seven days after setting to evaluation of the hydrophilic maintenance nature shown in the example mentioned later maintained not less than 30 degrees, and photocatalyst activity evaluation. In the case of the tunic of the crystalline titanium oxide simple substance which has a photocatalyst effect which does not reheat a conventional method, while ultraviolet rays are irradiated, a photocatalyst effect is active, but. If subsequent ultraviolet rays are intercepted even if hydrophilization is once carried out by UV irradiation, once ultraviolet rays are no longer irradiated, will return for a short time comparatively at the original hydrophobicity of titanium oxide, but. Whether ultraviolet rays are intercepted or the titanium oxide film obtained by the method of this invention becomes a situation where ultraviolet ray intensity is weak, a long period of time has the feature which has the performance which maintains hydrophilic nature. It has the high durability in which the photocatalyst coating covering glass obtained by the method of this invention maintained balance by various functions which solar reflectance (film surface side) also has 20 to 30% of outstanding heat ray reflection performance, and also have the above-mentioned hydrophilic nature and antifouling property.

[0015]

[Example]Hereafter, an example explains this invention concretely. However, this invention is not limited by these examples. The following evaluation was performed about the obtained sample supposing the antifouling window material used for the exterior, such as a building. Abrasion resistance, acid resistance, and alkali resistance were evaluated based on A of JIS-R-3221 (heat reflective glass). An evaluation result is shown in Table 1.

[0016](Valuation method)

** Based on the wear-resistant test method of wear-resistant JIS R 3221 statement, wear wheel CS-10F and load 500gf estimated the haze value by the Taber's abrasion resistance test. Early haze value H_0, haze value H_{100} of 100 times after, and the haze value of 200 times after is [H_{200} of evaluation] $H_0<=H_{100}<=H_{200}$, The case where Hays variation **H of the first stage and 200 times after (**H=$H_{200}-H_0$) was **H<=4% was considered as success (O), and $H_{100}>H_{200}$ or **H>4% of a thing was made into rejection (x).

[0017]** Based on the acid-proof test method of acid-proof JIS R 3221 statement, it wiped away and dried in flannel in the stream after 24-hour immersion to 1 N of chloride kept at 23 ** **2 **, and appearance was evaluated. Evaluation considered the case where there was no remarkable appearance change as success (O), and when remarkable discoloration or crack entered, that in which the film exfoliated was taken as rejection (x).

[0018]** The alkali resistance test method of alkali-proof JIS R 3221 statement. It wiped away and dried in flannel in the stream after 24-hour immersion to the 1-N sodium hydroxide solution kept at 23 ** **2 **, and appearance was evaluated. Evaluation considered the case where there was no remarkable appearance change as success (O), and when remarkable discoloration or crack entered, that in which the film exfoliated was taken as rejection (x).

[0019]** The degree of separation of stearic acid estimated the photocatalyst activity of the capability to disassemble the dirt with which the photocatalyst activity surface was stained. Paragon 1000 (FT-IR spectral device by Perkin-Elmer) is used for a valuation method, The peak intensity (absorbance A) resulting from the C-H stretching vibration of the stearic acid which appears from 2910-cm^{-1} to 2920-cm^{-1}, After irradiating with A_0 and ultraviolet rays for 1 hour at the time of A_b before stearic acid spreading, and stearic acid spreading, it asks about A_1, respectively, Variation of peak intensity: $\{(A_0-A_b)-(A_1-A_b)\}$ x1000 was computed and it was considered as the degree of separation of stearic acid (photocatalyst activity becomes high, so that a stearic acid degree of separation is large).

[0020]The sample was immersed in the 3wt% stearic acid-ethanol solution, and spreading to the sample of stearic acid was performed by pulling up in sec in 8 mm /. Ultraviolet ray intensity of the

sample surface was made the source of ultraviolet rays with 4mW[/cm] ^{2} (365 nm) using black light floor line15BLB (product made from Toshiba Electrical and electric equipment). Evaluation considered the case where the variation of said peak intensity was ten or more as success, and made less than ten the rejection.

[0021]** Also as for hydrophilic nature being maintained to some extent, the surface by which hydrophilization was once carried out in addition to photocatalyst activity was important for hydrophilic maintenance nature antifouling property, and the angle of contact over water after neglecting it for seven days in the laboratory under the environment below ultraviolet-ray-intensity 1 microwatt/cm ^{2} (365 nm) estimated hydrophilic maintenance nature after sample production. The angle of contact theta of seven days after considered theta<=30 degrees as success (O), and evaluation showed theta> 30 degrees by rejection (x).

[0022](Example 1) Dipropoxybis acetylacetonato titanium (made by Nippon Soda Co., Ltd.) as an organic titanium compound 33.2 g, 2.0g, 2, and 4 pentanedione (made by Kishida Chemical Co., Ltd.) were mixed for the 2 ethyl 1 and 3 hexandiol (made in Tokyo Chemicals), 61.6 g was mixed for 3.2 g and dichloromethane (made by Tokuyama), it stirred enough, and coating liquid was obtained. Next, a 6-mm-thick float glass board (soda lime silicate glass) is used as a substrate at 300 mm x 300 mm often washed, After having made it stay for 8 minutes into the electric furnace set as 600 **, having picked out the glass plate from the electric furnace, carrying out the 30g spray of the coating liquid promptly and carrying out a pyrolysis on the glass substrate surface, it once cooled to the room temperature and the uniform titanium oxide film was obtained. When the refractive index of the obtained film was measured by the ellipsomter (DVA-36-smooth S form by Mizojiri Optical Co., Ltd.), it was 2.30, and the thickness similarly measured by the ellipsomter was 67 nm. Measuring the reflection by the side of a film surface with the spectrophotometer (U4000 type by Hitachi, Ltd.), the light reflectance based on JIS-R-3016 was 27.2% in solar reflectance at 31.7%. Next, crystalline titanium oxide membrane was obtained by putting the titanium oxide film covering glass into the muffle electric furnace FP41 type (made by Yamato Scientific Co., Ltd.) set as 600 ** for 15 minutes, and carrying out a reheating process to it. The crystal of the obtained titanium oxide was a high crystalline anatase form crystal.

[0023]As a result of the method shown above estimating the obtained glass with photocatalyst membrane, as shown in Table 1, the sample of photocatalyst activity is greatly [as 14 degrees] good, and is 25 degrees also about hydrophilic maintenance nature, and even if it uses it for the window material (the film side. outdoor side) of a building, it has sufficient high durability. The refractive index of the photocatalyst membrane after reheating, thickness, light reflectance, and solar reflectance were with the numerical value before reheating. when the outdoor exposure of the sample glass substrate independent [same] which does not have a tunic as a reference in addition was actually carried out, dirt was attached and condition was evaluated, compared with the glass substrate to which a tunic is not attached, it was markedly alike, and has checked that there was little dirt.

[0024]

[Table 1]

ｻﾝﾌﾟﾙNo	耐摩耗性	耐酸性	耐ｱﾙｶﾘ性	光触媒活性	親水維持性	総合評価
実施例1	○	○	○	14	24.9	合格
実施例2	○	○	○	18	30.0	合格
実施例3	○	○	○	11	28.1	合格
比較例1	○	○	○	0	59.8	不合格
比較例2	○	○	○	0	57.5	不合格
比較例3	○	○	○	5	48.6	不合格
比較例4	○	○	○	1	47.3	不合格

[0025](Example 2) As an organic titanium compound, 33.2 g was mixed for dipropoxybis acetylacetonato titanium (made by Nippon Soda Co., Ltd.), 66.8 g was mixed for dichloromethane (made by Tokuyama), it stirred enough, and coating liquid was obtained. Next, after carrying out the 20g spray of the coating liquid like Example 1 and carrying out a pyrolysis on a glass plate, it cooled and the uniform titanium oxide film was obtained. The refractive index of the obtained film was 2.16 and thickness was 67 nm. Light reflectance was 28.9% and solar reflectance was 24.4%. Next, the

reheating process of the glass plate with a titanium oxide film was carried out like Example 1, and the second good crystalline titanium oxide film was obtained. As a result of the method shown above estimating the obtained glass with photocatalyst membrane, the result of having excelled like Example 1 was obtained.

[0026](Example 3) After having made it stay for 8 minutes into the electric furnace set as 630 ** with the same coating liquid as Example 1, having picked out the glass plate from the electric furnace, carrying out the 25g spray of the coating liquid promptly and carrying out a pyrolysis on a glass plate, it cooled and the uniform titanium oxide film was obtained. The refractive index of the obtained film was 2.28 and thickness was 64 nm. Light reflectance was 32.1% and solar reflectance was 27.1%. Next, the reheating process of the glass plate with a titanium oxide film was carried out like Example 1, and the good crystalline titanium oxide film was obtained. As a result of the method shown above estimating the obtained glass with photocatalyst membrane, the result of having excelled like Example 1 was obtained.

[0027](Comparative example 1) After having made it stay for 8 minutes into the electric furnace set as 450 ** with the same coating liquid as Example 1, having picked out the glass substrate from the electric furnace, carrying out the 40g spray of the coating liquid promptly and carrying out a pyrolysis on a glass substrate, it cooled and the uniform titanium oxide film was obtained. The refractive index of the obtained film was 1.80 and thickness was 16 nm. Light reflectance was 9.3% and solar reflectance was 5.7%. Next, reheating treatment of the glass plate with a titanium oxide film was carried out like Example 1. As a result of the method shown above estimating the obtained glass with photocatalyst membrane, as shown in Table 1, 0 degree and activity did not have photocatalyst activity, and hydrophilic maintenance nature was also as large as about 60 degrees, and for using it as a window material (the film side. outdoor side) of a building, there was a problem in endurance.

[0028](Comparative example 2) Only reheating treatment was excluded about the glass plate with a titanium oxide film of Example 2. As a result of the method shown above estimating the obtained glass with photocatalyst membrane, as shown in Table 1, photocatalyst activity did not have 0 degree and activity, and hydrophilic maintenance nature of the sample was also as large as about 58 degrees, and there was a problem in using it as a window material (the film side. outdoor side) of a building at endurance.

[0029](Comparative example 3) About the glass plate with a titanium oxide film of Example 2, reheating treatment was carried out at 700 **. As a result of the method shown above estimating the obtained glass with photocatalyst membrane, as shown in Table 1, The 15g spray of the coating liquid 1 the photocatalyst activity of 8 degrees and activity is small, and large [a sample] hydrophilic maintenance nature as about 49 degrees and same as Example (comparative example 4) 1 in which a problem was in using it as a window material (the film side. outdoor side) of a building at endurance is carried out, The pyrolysis was used on the glass plate and the uniform titanium oxide film was obtained. The refractive index of the obtained film was 2.32 and thickness was 30 nm. Light reflectance was 22.0% and solar reflectance was 17.3%. Next, reheating treatment of the glass plate with a titanium oxide film was carried out like Example 1.

[0030]

[Effect of the Invention]As mentioned above, according to the manufacturing method of the multifunctional photocatalyst coating covering glass of this invention. It is what provides the multifunctional photocatalyst membrane covering glass which had the improvement in visibility by the antifouling property and hydrophilic nature into which the contamination organic substance which makes a photocatalyst activity function reveal and adheres to the glass substrate surface is made to disassemble effectively, without spoiling the heat ray reflex function and endurance which are equipped conventionally, Since it has endurance sufficient also by the operating environment which requires endurance which uses photocatalyst membrane for the outdoor side, such as a windowpane of a building, and a windowpane for vehicles, hydrophilic nature, antifouling property by a photocatalyst, etc., it is especially suitable.

[Translation done.]